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C→N Migrations of the ethoxycarbonyl group in reactions of *ortho*-substituted aryl isocyanates with the 1,3-zwitterion derived from triisopropylphosphine and ethyl 2-cyanoacrylate

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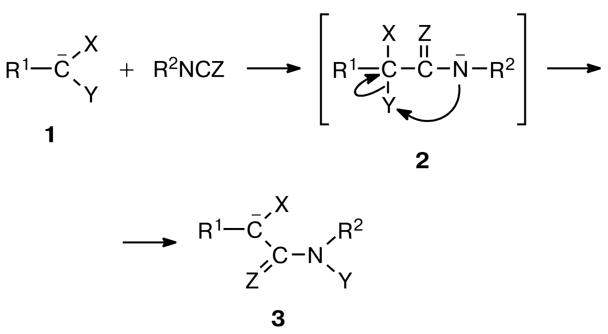
The reactions of *meta—para*-substituted aryl isocyanates with phosphorus-containing 1,3-zwitterions, which proceed with the C→N migration of the CO_2Et group to form the corresponding carbamates, were extended to *ortho*-substituted aryl isocyanates. The influence of the steric and electronic effects of the *ortho* substituents in the aromatic rings of aryl isocyanates on the ease of this rearrangement is qualitatively considered.

Key words: C→N migration of the ethoxycarbonyl group, aryl isocyanates, *ortho* effect, phosphorus-containing zwitterions.

In 1995, it was found[1,2] that the reactions of phenyl isocyanate with phosphorus-containing zwitterions, which are generated by the reactions of tripropylphosphine or hexaethylphosphorous triamide with methyl or ethyl 2-cyanoacrylate, involve the migration of the alkoxycarbonyl group from the carbon atom to the nitrogen atom (Scheme 1). Later on, it was demonstrated that this rearrangement has a rather general character. Not only phosphorus-containing 1,3-zwitterions[3—7] but also free mono- and bis-carbanions[8—10] and nitrogen ylides[11,12] reacted according to the same scheme of the insertion of isocyanates at the C—C bond. Methyl isocyanate, phenyl isothiocyanate, 1-naphthyl isocyanate, *meta*- or *para*-substituted phenyl isocyanates, and diisocyanates were successfully used as heterocumulenes in these transformations.[3—12]

Scheme 1



R^1 = Ph, Py, isoquinolyl, $Pr^n_3P^+CH_2$, $Pr^i_3P^+CH_2$, $Bu^n_3P^+CHPh$, $(Et_2N)_3P^+CH_2$
R^2 = Me, Ph, *m*-Tol, 1-naphthyl, 4-ClC_6H_4, 3,4-$Cl_2C_6H_3$, 4-$O_2NC_6H_4$
X = CN, CO_2Et; Y = CO_2Me, CO_2Et, C(O)Me; Z = O, S

By contrast, 2,6-dichlorophenyl and 2,4,6-trichlorophenyl isothiocyanates reacted with zwitterion **1a** according to another scheme to give adducts **4** (Scheme 2)[13] due, apparently, to the fact that two *ortho*-chlorine atoms hinder the formation of the expected carbamates of type **3** (the reaction of phenyl isothiocyanate with zwitterion **1a** proceeded as a traditional rearrangement[6] through the C→N migration of the ethoxycarbonyl group). This gave impetus to a detailed study of the reactions of the *ortho*-substituted phenyl isocyanates with carbanions.

The *ortho* substituents in aryl isocyanates are responsible for a decrease in the reactivity of these compounds with respect to different reagents.[14] Apparently, this is associated both with the electronic effect and spatial shielding of the reaction centers of the species involved in the reaction. According to Scheme 1, the second step of the reaction involves the nucleophilic attack of the nitrogen atom of mesomeric N-anion **2** on the carbonyl car-

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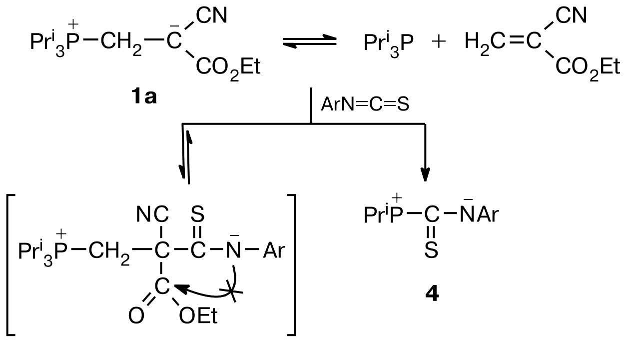
Scheme 2



Ar = 2,6-$Cl_2C_6H_3$, 2,4,6-$Cl_3C_6H_2$

bon atom of the alkoxycarbonyl or acetyl group. The rate of this step can also be sensitive to the steric effect of *ortho* substituents in the aromatic ring. The importance of the steric effects in the transformations under consideration was confirmed by comparing the reactivities of 2,6-dimethyl and 3,5-dimethylphenyl isocyanates toward zwitterion **1a** (Scheme 3). According to the ^{31}P NMR spectroscopic data, the reactions with isocyanate containing the *ortho*-methyl groups afforded the target carbamate **5a** in only 4.7% yield, whereas the reaction (performed under analogous conditions) of isocyanate containing the methyl groups in the *meta* positions with respect to the isocyanate fragment gave rise to carbamate **5b** in a yield of up to 95%. The structure of the latter compound (Fig. 1) was established by X-ray diffraction analysis (see below).

Scheme 3

$Pr^i_3P^+CH_2C^-(CN)CO_2Et \xrightarrow{ArNCO}$
1a

$\longrightarrow Pr^i_3P^+CH_2C^-(CN)N(Ar)CO_2Et$
5a,**b**

Ar = 2,6-$Me_2C_6H_3$ (**a**), 3,5-$Me_2C_6H_3$ (**b**)

The yields of the compounds were estimated by ^{31}P NMR spectroscopy. The actual yields (see the Experimental section) were much lower, because it was necessary to purify the target compounds from impurities, which were generated through transformations of aryl isocyanates used in an excess.

We performed a systematic study of the transformations of phosphorus-containing zwitterion **1a** in the reactions with different aryl isocyanates, including compounds, which bear atoms or groups exhibiting different electronic and steric effects as the *ortho* substituents in the phenyl ring (Scheme 4).

The reaction performed according to Scheme 4 gave conclusive results. In the ^{31}P NMR spectra of the reaction mixtures at room temperature, the intensity of the signal for the phosphorus atom of the resulting carbamate **6** (δ 41±0.5) increases with time, the intensity of the signal for the phosphorus atom of the starting zwitter-

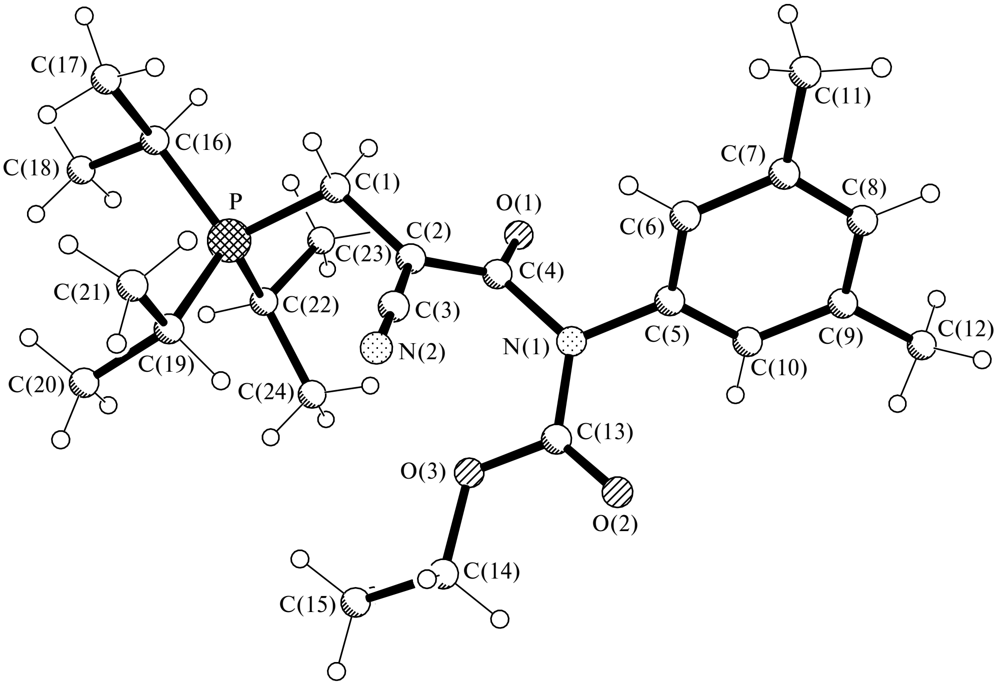
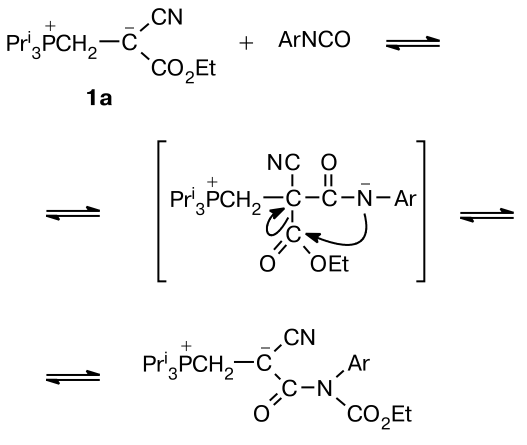


Fig. 1. Molecular structure of zwitterion **5b**.

Scheme 4



6a—j, **7—9**

Ar = 2-XC_6H_4 (**6a—j**), 1-naphthyl (**7**), 2,4-$Me_2C_6H_3$ (**8**), Ph (**9**)
6: X = F (**a**), Cl (**b**), Br (**c**), I (**d**), Me (**e**), Et (**f**), Pr^i (**g**), Ph (**h**), CF_3 (**i**), MeO (**j**)

ion **1a** (δ 38.7) decreasing in parallel. In addition to these two main signals, the ^{31}P NMR spectra generally have signals of triisopropylphosphine (δ 20.8) and its oxide (δ 58.8). Triisopropylphosphine is generated through dissociation of zwitterion **1a** into the starting reagents.[13] The conversion of **1a** into carbamates **6** at room temperature depends only on the time of storage of the reagents in a solution in CH_2Cl_2 in the presence of a two- to fivefold excess of aryl isocyanate. For example, according to the ^{31}P NMR spectroscopic data, the reactions of the compound with X = Et afforded the corresponding carbamate **6f** in 4, 19, and 55.9% yields after 1, 4, and 17 days, and the yield was higher than 90% after 40 days. The same compound was obtained in ~80% yield (^{31}P NMR spectroscopic data) upon heating of a mixture of the reagents in toluene at 100 °C for 6 h. Hence, ^{31}P NMR spectroscopy enables one to estimate the conversion under the standard conditions from the yields of the corresponding carbamates depending on the properties of the substituent X (Table 1) by performing the reactions according to Scheme 4 at room temperature for 100 h (50% solution in CH_2Cl_2) in the presence of a twofold excess of isocyanate. In this case, the degree of selectivity of the process can be estimated as the ratio (in %) of the sum of integral intensities of the ^{31}P signals of the starting zwitterion **1a** and the resulting corresponding carbamate **6** to the overall intensity of the signals for the phosphorus atoms in the ^{31}P NMR spectrum of the reaction mixture. Apparently, the closer is this value to 100%, the higher is the selectivity of the process. At room temperature, the selectivity slightly decreases with time. For example, in the case of X = Et, the reaction mixture contained 55.9% of carbamate **6f** and 38.9% of zwitterion **1a** after 17 days, whereas 80.1% of carbamate **6f** and 3.9% of zwitterion **1a** were present in the reaction mixture after 6 weeks. A comparison of the reactions of phenyl isocyanate and *ortho*-substituted aryl isocyanates proceeding according to Scheme 4 led to the conclusion that all *ortho* substituents, except for the fluorine atom, hinder the formation of carbamates **6**. It can be noted that an increase in the size of the substituent X in the series of related compounds (X = F, Cl, Br, or I; X = Me, Et, or Pr^i) hinders the insertion of the isocyanate molecule at the C—C bond of the starting zwitterion **1a**. Evidently, the electronic factors, which sometimes compensate the hindering steric *ortho* effect of the substituent, also play a particular role. For example,

Table 1. Relationship between the structures of aryl isocyanates **6—9** and the yields (^{31}P NMR spectroscopic data) of the corresponding carbamates generated according to Scheme 4 (100 h, ~20 °C, CH_2Cl_2)

Compound	Ar	Yield (%)	*S* (%)	V_X	r_X/Å	σ*	σ$^+$
6a	FC_6H_4	95.4	96.6	0.27	0.64	3.1	–0.24
6b	ClC_6H_4	85.9	99.1	0.55	0.99	2.68	–0.15
6c	BrC_6H_4	80.0	98.1	0.65	1.14	2.63	–0.11
6d	IC_6H_4	72.1	99.0	0.78	1.33	2.22	–0.13
6e	MeC_6H_4	19.9	98.3	0.52	—	0.00	–0.17
6f	EtC_6H_4	19.0	99.2	0.56	—	–0.10	–0.17
6g	$Pr^iC_6H_4$	10.8	98.1	0.76	—	–0.19	–0.16
6h	PhC_6H_4	25.0	96.2	0.57	—	0.60	–0.19
6i	$CF_3C_6H_4$	54.0	97.0	0.91	—	2.49	—
6j	$MeOC_6H_4$	5.0	99.1	—	—	1.67	–0.64
7	1-Naphthyl	82.5	100.0	—	—	—	—
8	2,4-$Me_2C_6H_3$	19.5	98.7	0.52	—	0.00	–0.17
9	H	98.0	97.2	0.00	—	—	—

Note. The following notations are used: *S* is the degree of selectivity (see the text), V_X is the volume of the substituent X according to Charton,[16] r_X is the covalent radius[17] of the X substituent, σ* and σ$^+$ are the electronic and resonance characteristics[18] of the substituent, respectively.

in spite of the larger size of the CF_3 group (compared to the methyl substituent), *o*-trifluoromethylphenyl isocyanate reacted with zwitterion **1a** faster than *o*-xylyl isocyanate. The steric factors alone are very unlikely to account for the fact that the transformations of *o*-methoxyphenyl isocyanate (according to Scheme 4) proceed with considerable difficulty.

Carbamate **3** was much less readily produced in the reactions of carbanions **1** with cyclohexyl isocyanate, which was used instead of phenyl isocyanate. An analogous effect has been observed earlier[12] in the study of the analogous reactions of isocyanates with pyridinium ylide derived from malonic ester. In the present study, we found that phenyl isocyanate reacted with zwitterion **1a** to give carbamate **9** in 98% yield at room temperature after four days, whereas the reaction of cyclohexyl isocyanate under the same conditions afforded the corresponding carbamate **10** in only 34% yield (according to the ^{31}P NMR spectroscopic data; see Scheme 5).

Scheme 5

$$\mathbf{1a} + \mathrm{RNCO} \longrightarrow \mathrm{Pr^i_3P^+CH_2C^-(CN)C(O)N(CO_2Et)R}$$

R = Ph (**9**), *cyclo*-C_6H_{11} (**10**)

The three-dimensional structures of carbamates **9** (Fig. 2) and **10** (Fig. 3) were established by X-ray diffraction analysis (see below).

The interpretation of the effect of the substituent X on the completeness of the reaction following Scheme 4 is hindered by the fact that both steps of the reactions according to Schemes 1 and 4 are reversible. The reversibility is most clearly manifested in the reactions producing carbamates **3** from isocyanates and pyridinium or isoquinolinium ylides derived from malonic ester.[11,12] Heating of either dry carbamate **3** generated from pyridinium ylide or a solution of **3** in acetone or $CDCl_3$ rapidly led to decomposition of carbamate **3** to the starting pyridinium ylide **1** and an isocyanate polymer. Carbamates **3** prepared from ethyl phenylcyanoacetate also rather readily underwent analogous decomposition.[10] Organophosphorus carbamates **3** and zwitterions **6** under consideration are more stable. Crystalline carbamates **6** remained unchanged indefinitely, whereas storage of a solution of carbamate **6c** in CH_2Cl_2 for several months gave rise to trimer **11** of the starting 2-bromophenyl isocyanate **6c**, which is indicative of decomposition of the carbamate to yield 2-bromophenyl isocyanate. The resulting zwitterion **1a** was also transformed into a number of products,[13] in particular, it dissociated to triisopropylphosphine and ethyl

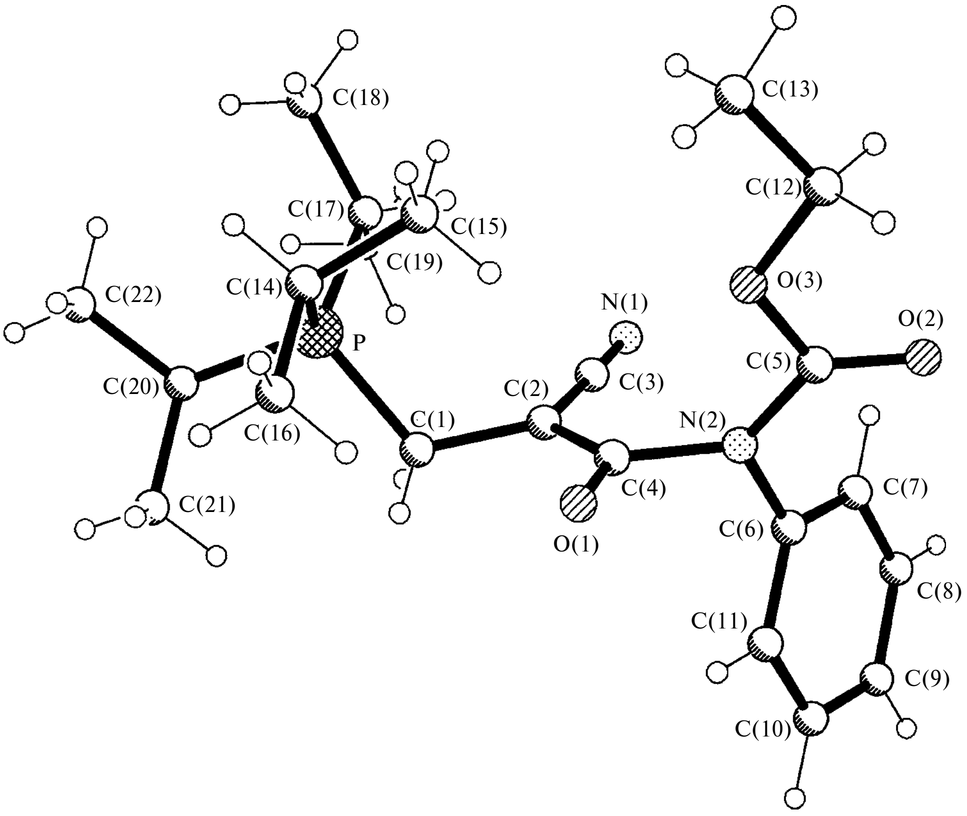


Fig. 2. Molecular structure of zwitterion **9**.

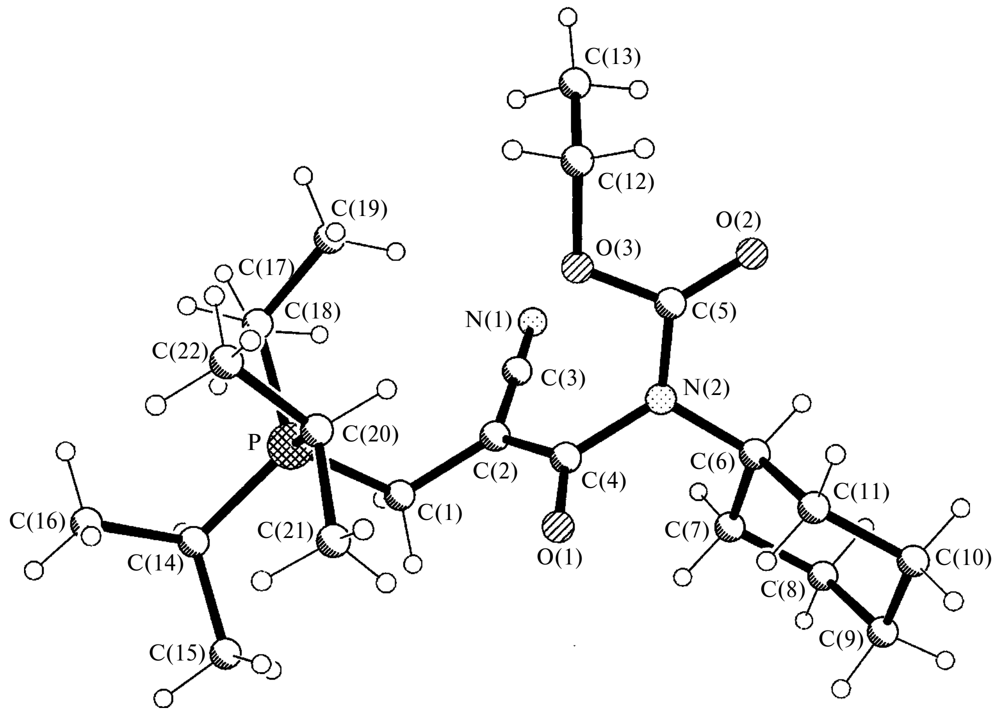


Fig. 3. Molecular structure of zwitterion **10**.

2-cyanoacrylate. The crystal structure of trimer **11** of 2-bromophenyl isocyanate (Fig. 4) was established by X-ray diffraction analysis. There are two crystallographically independent molecules **11** and one CH_2Cl_2 molecule per asymmetric unit. The ring of the molecule is virtually planar (to within 0.029 Å [0.015 Å]; the characteristics of the second molecule **11** are given in brackets). The deviations of the atoms from the mean plane vary from −0.05 Å (C(1)) to 4.5 Å (N(1)) [from −0.023 Å (N(2)) to 0.033 Å (C(2))]. The dihedral angles be-

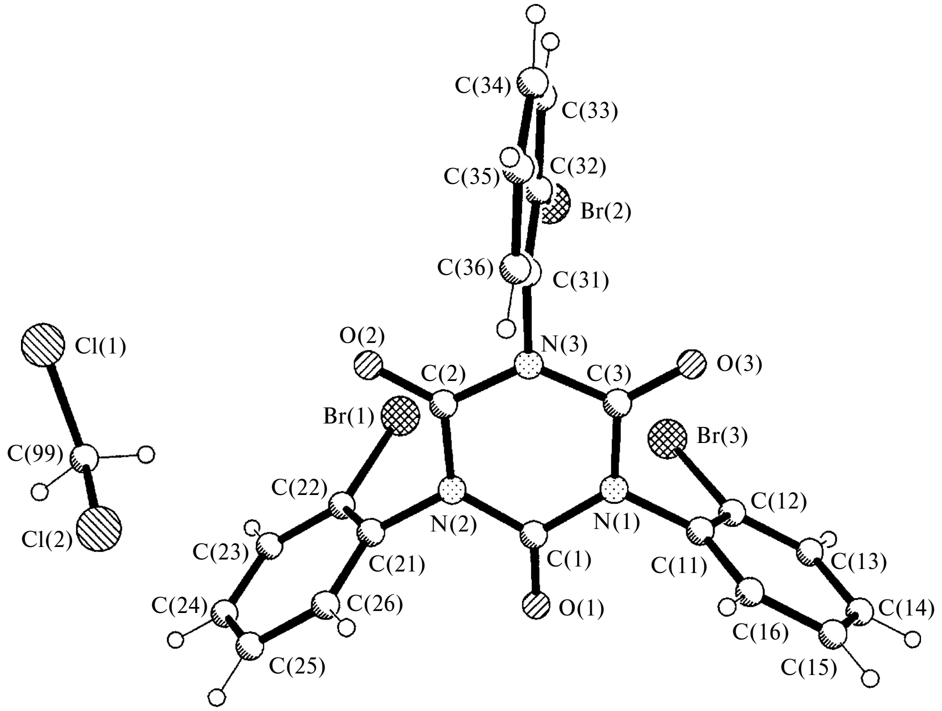


Fig. 4. Molecular structure of trimer **11** of 2-bromophenyl isocyanate (adduct with CH_2Cl_2).

tween the bromophenyl rings and the central ring are in the range of 65.7°—97.6°. The endocyclic C—N bond lengths [1.387(4)—1.400(4) Å] are typical of such systems.[15] This is also true for the C=O bond lengths [1.195(4)—1.212(4) Å] and exocyclic C—N bond lengths [1.441(4)—1.457(4) Å].

Carbamates **6e**,**f** and **7** (the synthesis of the latter has been described earlier[6]) were studied by X-ray diffraction analysis to reveal the steric hindrances to the rotation of the aromatic fragment about the C—N bond due to the presence of the *ortho* substituents. According to the ^{1}H NMR spectroscopic data and results of X-ray diffraction study, the protons of the methyl and ethyl groups in the *ortho* positions of the aryl substituents in compounds **6e** and **6f** and the *peri*-proton of the 1-naphthyl substituent in compound **7** hinder free rotation of the aryl fragment about the N—C bond. The atropoisomerism of carbamates **6** will be quantitatively discussed elsewhere.

Since compounds **5b**, **9**, and **10** differ only by the substituent at the nitrogen atom, they are discussed collectively. The bond lengths and bond angles are given in Tables 2 and 3, respectively. The crystal of compound **9** contains two crystallographically independent molecules (A and B). In compounds **5b** and **9**, the negatively charged C(2) atoms deviate from the planes of the substituents bound to these atoms by 0.029 and 0.057 Å, respectively. The angles at the C(2) atom are close to the ideal value of 120° [117.8(3)° and 121.4(3)°]. In all the compounds under consideration, the C(1)—C(2), C(2)—C(3), and C(2)—C(4) bond lengths (see Table 2) are in agreement with the earlier results.[4] It should be noted that the C(2)—C(3) bond lengths are substantially smaller than the standard (C)—C≡N bond length (1.470 Å). The C(3)≡N(1) triple bond lengths are larger than the standard value (1.136 Å).[4] The C(4)=O(1) double bond lengths are larger than the standard value for amides (1.231 Å).[4] These facts are indicative of particular delocalization of the negative charge in the N≡C—C—C=O fragment. The P—C(1) bond lengths are rather constant (see Table 2). The P—CMe$_2$ bond lengths in compound **9** are 1.820(4) and 1.830(4) Å.

Table 2. Selected bond lengths (*d*) in compounds **5b**, **9**, and **10**

Bond	*d*/Å			
	5b	**9**		**10**
		A	B	
P—C(1)	1.8220(9)	1.818(3)	1.818(4)	1.8186(11)
C(1)—C(2)	1.5077(13)	1.513(5)	1.509(5)	1.5086(14)
C(2)—C(3)	1.4128(14)	1.404(5)	1.413(6)	1.4001(15)
C(2)—C(4)	1.3908(14)	1.393(5)	1.380(6)	1.3957(14)
C(3)—N(1)	1.1519(15)	1.160(5)	1.151(6)	1.1557(15)
C(4)—N(2)	1.4722(12)	1.483(5)	1.484(5)	1.4636(13)
C(4)—O(1)	1.2387(12)	1.239(4)	1.244(5)	1.2363(13)

Table 3. Selected bond angles (ω) in compounds **5b**, **9**, and **10**

Angle	ω/deg			
	5b	**9**		**10**
		A	B	
P—C(1)—C(2)	117.16(7)	117.4(3)	117.0(3)	115.95(7)
C(1)—C(2)—C(4)	119.91(9)	120.5(3)	120.1(4)	118.40(9)
C(2)—C(4)—N(2)	116.52(8)	113.4(3)	114.6(4)	115.72(9)
C(4)—N(2)—C(5)	126.33(8)	123.6(4)	119.3(4)	121.01(9)

The P—C(1)—C(2) angle formed by the positively charge phosphorus atom and the negatively charged carbon atom (see Table 3) is larger than the expected value, which may be associated with the steric factors. The C(3)—C(2)—C(4)—N(2) torsion angles vary from −4.8° for compound **9** to 3.7° for compound **10**. The C(6)—N(2)—C(5)—O(2) torsion angles are −3.0° and 10.0° for compounds **9** and **10**, respectively. The phosphorus atom has a tetrahedral configuration characterized by the angles of 106.16(16)° and 115.36(5)° for compounds **9** and **5b**, respectively.

The procedures developed for the synthesis of phosphorus-containing carbamates bearing *ortho*-substituted aromatic fragments at the nitrogen atom substantially extend the field of application of the rearrangement involving the C→N migration of the alkoxycarbonyl group.

Experimental

The NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400.13 MHz for ^{1}H, 161.97 MHz for ^{31}P, 100.61 MHz for ^{13}C, and 376.49 MHz for ^{19}F; the chemical shifts (δ) were measured with respect to Me$_4$Si (^{1}H and ^{13}C) or 85% H$_3$PO$_4$ (^{31}P). The reactions were carried out under dry nitrogen. The solvents were thoroughly purified and dried before use. The yields, melting points and data from elemental analysis are given in Table 4. The results of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy are presented in Table 5.

Synthesis of compounds 6a—d and 9 (general procedure).[6] A mixture of zwitterion **1a** (0.5 g, 0.0017 mol) and the corresponding aryl isocyanate (2 equiv.) in CH$_2$Cl$_2$ (1 mL) was kept at room temperature (~20 °C) for 4 days. According to the ^{31}P NMR spectroscopic data, the reaction mixtures each contained primarily the reaction product and the starting zwitterion (see Table 1). Then the reaction mixture was poured into a tenfold excess of dry hexane. The precipitate that formed was twice washed with hexane and recrystallized from a Me$_2$CO—Et$_2$O—CH$_2$Cl$_2$ mixture or THF.

The reaction of zwitterion 1a with 2,6- or 3,5-dimethylphenyl isocyanates. A mixture of zwitterion **1a** (0.5 g, 0.0017 mol) and the corresponding aryl isocyanate (2 equiv.) in CHCl$_3$ (1 mL) was heated at 60 °C for 3 h. The product of the reaction with 3,5-dimethylphenyl isocyanate was treated according to a procedure described above, but crystallized at the interface (Me$_2$CO—Et$_2$O) using hexane.

Table 4. Yields, melting points, and elemental analysis of the compounds synthesized

Compound	Yield (%)	Molecular formula	Found / Calculated (%)			M.p./°C
			C	H	N	
6a	44.7	$C_{22}H_{32}N_2O_3PF$	62.84 62.56	7.77 7.58	6.61 6.63	145.0—146.0
6b	56.1	$C_{22}H_{32}N_2O_3PCl$	60.32 60.20	7.37 7.29	6.34 6.38	169.0—170.0
6c	34.7	$C_{22}H_{32}N_2O_3PBr$	54.31 54.65	6.59 6.62	5.45 5.79	170.0—171.0
6d	24.8	$C_{22}H_{32}N_2O_3PI$	49.56 49.81	6.01 6.03	5.15 5.28	170.0—170.5
6e	34.3	$C_{23}H_{35}N_2O_3P$	65.69 66.03	8.42 8.37	6.54 7.00	177.0—178.0
6f	23.6	$C_{24}H_{37}N_2O_3P$	66.34 66.6	8.44 8.56	6.33 6.48	151.0—151.5
6g	21.8	$C_{25}H_{39}N_2O_3P$	67.12 67.26	8.53 8.74	6.17 6.27	164.0—165.0
6h	22.7	$C_{28}H_{37}N_2O_3P$	69.55 70.0	7.91 7.71	5.48 5.83	106.0—107.5
6i	19.7	$C_{23}H_{32}N_2O_3PF_3$	58.22 58.47	6.56 6.78	5.77 5.97	110.0—111.0
6j	12.7	$C_{23}H_{35}N_2O_4P$	63.03 63.59	7.88 8.06	6.87 6.45	173.0—174.0
9	26.0	$C_{24}H_{37}N_2O_3P$	65.9 66.6	8.37 8.56	6.26 6.48	171.0—171.5
10	27.8	$C_{22}H_{38}N_2O_3P$	64.34 64.54	9.00 9.29	6.66 6.84	143.0—144.0

Carbamates 6e,h,i and 8. A mixture of zwitterion **1a** (0.5 g, 0.0017 mol) and the corresponding aryl isocyanate (2 equiv.) in CH_2Cl_2 (1 mL) was stored in a closed vessel for 30 days. Then the mixtures were treated as described in the general procedure.

Carbamate 6f. A mixture of zwitterion **1a** (1.0 g, 0.0035 mol) and 2-ethylphenyl isocyanate (1.54 g, 0.01 mol) in $CHCl_3$ (2 mL) was heated at 60 °C for 10 h. The cooled reaction mixture was washed three times with hexane and then stirred with activated carbon in Me_2CO for 3 h. The solution was filtered, the solvent was removed, and the residue was crystallized repeatedly from a Me_2CO—Et_2O—hexane mixture. Compound **6f** was obtained as colorless crystals.

Table 5. Data from ^1H, ^{13}C, and ^{31}P NMR spectroscopy for the compounds synthesized

Compound	δ (*J*/Hz)		
	^{13}C	^1H	^{31}P
6a	—	1.21 (t, 3 H, $CH_2\underline{CH}_3$, $^3J_{H,H} = 7.1$); 1.33 (dd, 18 H, $(CH_3)_2CH$, $^3J_{P,H} = 15.2$, $^3J_{H,H} = 7.2$); 2.66 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.3$, $^3J_{H,H} = 7.2$); 3.15 (d, 2 H, $C\underline{H}_2P^+$, $^2J_{P,H} = 8.5$); 4.14 (q, 2 H, $C\underline{H}_2CH_3$, $^3J_{H,H} = 7.1$); 7.09 (m, 2 H); 7.21 (m, 1 H); 7.38 (m, 1 H, C_6H_4)	40.97
6b	14.72 ($CH_2\underline{C}H_3$); 17.15 (d, $(\underline{C}H_3)_2CH$, $^2J_{P,C} = 3.3$); 17.49 (d, $\underline{C}H_2P^+$, $^1J_{P,C} = 44.1$); 20.74 (d, $Me_2\underline{C}H$, $^1J_{P,C} = 40.1$); 51.88 (C^-); 61.32 ($\underline{C}H_2CH_3$); 126.59 ($\underline{C}N$); 124.54, 127.91 (CHPh); 137.78, 139.69 (CPh); 154.20 ($CN\underline{C}O$); 168.05 ($C^-\underline{C}ON$)	1.25 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.1$); 1.49 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H} = 15.2$, $^3J_{H,H} = 7.2$); 2.75 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.6$, $^3J_{H,H} = 7.2$); 3.26 (d, 2 H, $C\underline{H}_2P^+$, $^2J_{P,H} = 8.1$); 4.23 (q, 2 H, $C\underline{H}_2CH_3$, $^3J_{H,H} = 7.1$); 7.18 (td, 1 H, Ph, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.5$); 7.24 (td, 1 H, Ph, $^3J_{H,H} = 7.1$, $^3J_{H,H} = 1.5$); 7.42 (dd, 1 H, Ph, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.5$); 7.50 (dd, 1 H, Ph, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.5$)	41.15

(*to be continued*)

Table 5 (*continued*)

Compound	δ (*J*/Hz)		
	^{13}C	^{1}H	^{31}P
6c	14.43 ($CH_2\underline{C}H_3$); 16.92 (s, $(\underline{C}H_3)_2CH$); 17.58 (d, CH_2P^+, $^1J_{P,C} = 43.8$); 20.55 (d, $(CH_3)_2\underline{C}H$, $^1J_{P,C} = 39.8$); 50.11 (C^-); 61.61 (CH_2CH_3); 124.20 ($\underline{C}N$); 127.48, 127.95, 129.85, 132.87 (CHPh); 126.64, 139.57 (CPh); 153.49 ($CN\underline{C}O$);166.87 ($C^-\underline{C}ON$)	1.16 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.2$); 1.39 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H} = 15.2$, $^3J_{H,H} = 7.3$); 2.67 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.4$, $^3J_{H,H} = 7.3$); 3.18 (br.d, 2 H, $C\underline{H}_2P^+$, $^2J_{P,H} = 6.8$); 4.16 (q, 2 H, $C\underline{H}_2CH_3$, $^3J_{H,H} = 7.2$); 7.02 (td, 1 H, Ph, $^3J_{H,H} = 8.0$, $^3J_{H,H} = 7.6$, $^4J_{H,H} = 1.4$); 7.19 (td, 1 H, Ph, $^3J_{H,H} = 7.8$, $^3J_{H,H} = 7.6$, $^4J_{H,H} = 1.4$); 7.40 (dd, 1 H, Ph, $^3J_{H,H} = 7.8$, $^4J_{H,H} = 1.4$); 7.51 (dd, 1 H, Ph, $^3J_{H,H} = 8.0$, $^4J_{H,H} = 1.4$)	40.86
6d	14.61 ($CH_2\underline{C}H_3$); 17.32 (d, $(\underline{C}H_3)_2CH$, $^2J_{P,C} = 3.2$); 17.76 (d, $(\underline{C}H_3)_2CH$, $^1J_{P,C} = 43.9$); 17.86 (d, $\underline{C}H_2P^+$, $^1J_{P,C} = 44.0$); 50.08 (d, C^-, $^2J_{P,C} = 3.2$); 61.95 ($\underline{C}H_2CH_3$); 126.98 ($\underline{C}N$); 128.34, 128.63, 129.51, 139.51 ($\underline{C}HPh$); 100.77, 143.14 (CPh); 153.38 ($CN\underline{C}O$); 166.91 (d, $^3J_{P,C} = 3.2$ ($C^-\underline{C}ON$)	1.17 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.2$); 1.40 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H} = 15.1$, $^3J_{H,H} = 7.3$); 2.67 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.5$, $^3J_{H,H} = 7.3$); 3.68 (br.s, 2 H, $\Delta\nu = 36.0$, $C\underline{H}_2P^+$); 4.15 (q, 2 H, $C\underline{H}_2CH_3$, $^3J_{H,H} = 7.2$); 6.86 (td, 1 H, Ph, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.4$); 7.25 (td, 1 H, Ph, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.4$); 7.37 (dd, 1 H, Ph, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.4$); 7.78 (dd, 1 H, Ph, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.4$)	41.04
6e	—	1.23 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.05$); 1.50 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H} = 15.2$, $^3J_{H,H} = 7.3$); 2.42 (c, 3 H, CH_3Ar); 2.75 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.4$, $^3J_{H,H} = 7.3$); 2.85 (q, 2 H, $C\underline{H}_2CH_3$, $^3J_{H,H} = 7.5$); 3.25 (d, $C\underline{H}_2P^+$, $^2J_{P,H} = 8.06$); 7.14—7.17 (m, 2 H); 7.20—7.22 (m, 1 H); 7.43—7.45 (m, 1 H)	41.33
6f	14.58 ($CH_2\underline{C}H_3$); 17.15 (d, $(\underline{C}H_3)_2CH$, $^2J_{P,C} = 3.3$); 17.90 (d, CH_2P, $^1J_{P,C} = 43.9$); 20.79 (d, $(CH_3)_2\underline{C}H$, $^1J_{P,C} = 40.1$); 50.24 (d, $\underline{C}CH_2P$, $^2J_{P,C} = 4.2$); 55.79 ($O\underline{C}H_3$); 61.27 ($\underline{C}H_2CH_3$); 126.84 ($\underline{C}N$); 155.76 ($N\underline{C}OO$); 168.25 ($^-C\underline{C}ON$); 111.99, 120.37, 127.86, 128.55 ($\underline{C}HPh$); 129.59, 154.35 (CPh)	1.27 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.5$); 1.50 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H} = 15.2$, $^3J_{H,H} = 7.3$); 2.76 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.4$, $^3J_{H,H} = 7.3$); 2.85 (q, 2 H, $C\underline{H}_2CH_3$, $^3J_{H,H} = 7.5$); 3.27 (br.d, $C\underline{H}_2P^+$, $^2J_{P,H} = 10.6$); 7.17 (td, Ph, $^3J_{H,H} = 7.7$, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.4$); 7.21 (td, Ph, 1 H, $^3J_{H,H} = 7.7$, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.3$); 7.26 (dd, Ph, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.4$); 7.45 (dd, 1 H, Ph, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.4$)	41.03
6g	14.77 ($CH_2\underline{C}H_3$); 17.10 ($(\underline{C}H_3)_2CH$); 17.80 (d, $\underline{C}H_2P$, $^1J_{P,C} = 43.7$); 20.84 (d, $(CH_3)_2\underline{C}HP$, $^1J_{P,C} = 40.1$); 27.75 ($(CH_3)_2\underline{C}H$); 50.16 (d, $\underline{C}^-CH_2P$, $^2J_{P,C} = 4.0$); 61.41 (CH_2CH_3); 127.20 (CN); 125.64, 125.99, 127.57, 129.37 (CHPh); 137.59, 147.62 ($\underline{C}Ph$); 154.61, $N\underline{C}OO$); 167.96 ($C^-\underline{C}ON$)	1.13 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.1$); 1.13 (d, 3 H, $^3J_{H,H} = 7.1$); 1.19 (d, $^3J_{H,H} = 7.1$, $(C\underline{H}_3)_2CH$); 1.40 (dd, 18 H, $(C\underline{H}_3)_2CHP$, $^3J_{P,H} = 14.9$, $^3J_{H,H} = 7.0$, $^3J_{H,H} = 7.0$); 2.65 (d.sept, 3 H, $(CH_3)_2C\underline{HP}$, $^3J_{H,H} = 7.0$, $^3J_{P,H} = 12.4$); 3.14 (dd, 2 H, $C\underline{H}_2P^+$, $^2J_{H,H} = 15.2$, $^2J_{P,H} = 8.4$); 3.20 (dd, 2 H, $C\underline{H}_2P^+$, $^2J_{H,H} = 15.2$, $^2J_{P,H} = 8.2$); 3.42 (sept, 1 H, $(CH_3)_2C\underline{H}$, $^2J_{H,H} = 15.2$, $^3J_{H,H} = 7.1$); 4.01 (br.s, 2 H, $(C\underline{H}_2CH_3)$; 7.06 (td, 1 H, Ph, $^3J_{H,H} = 7.7$, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.4$); 7.16 (td, 1 H, Ph, $^4J_{H,H} = 1.9$, $^3J_{H,H} = 7.7$, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.0$); 7.23 (dd, 1 H, Ph, $^3J_{H,H} = 7.7$, $^4J_{H,H} = 1.4$); 7.38 (dd, 1 H, Ph, $^3J_{H,H} = 7.7$, $^3J_{H,H} = 1.0$)	41.01
6h	14.28 ($CH_2\underline{C}H_3$); 17.16 (d, $(\underline{C}H_3)_2CH$, $^2J_{P,C} = 3.2$); 17.77 (d, CH_2P, $^1J_{P,C} = 43.7$); 20.70 (d, $(CH_3)_2\underline{C}H$, $^1J_{P,C} = 40.3$); 50.26 ($^-\underline{C}CH_2P$); 61.24 (CH_2CH_3); 127.06 (CN); 126.73, 126.86, 127.82, 130.48 (CHPh); 138.32, 139.82, 140.12 (CPh); 153.46, $N\underline{C}OO$); 168.52 ($C^-\underline{C}ON$)	0.92 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.1$); 1.48 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H} = 15.2$, $^3J_{H,H} = 7.2$); 2.72 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.5$, $^3J_{H,H} = 7.2$); 3.29 (br.s, 2 H, $C\underline{H}_2CH_3$, $\Delta\nu = 22.0$); 3.65 (br.s, 2 H, $C\underline{H}_2CH_3$); 7.80 (d, 2 H, Ph, $^3J_{H,H} = 7.3$); 7.24—7.40 (m, 7 H, Ph)	41.17

(*to be continued*)

Table 5 (*continued*)

Com-pound	δ (*J*/Hz)		
	^{13}C	^{1}H	^{31}P
6i*	14.33 ($CH_2\underline{C}H_3$); 17.09 (d, $CH(CH_3)_2$, $^2J_{P,C} = 1.7$); 17.92 ($\underline{C}H_2P$, $^1J_{P,C} = 44.1$); 20.70 (d, $(CH_3)_2\underline{C}H$, $^1J_{P,C} = 40.0$); 49.49 (d, C^-, $^2J_{P,C} = 3.8$); 61.77 ($\underline{C}H_2CH_3$); 126.07 ($\underline{C}N$); 120.07, 128.58, 138.20 ($\underline{C}Ph$); 127.31, 131.27, 132.15 (CH(Ph), CF_3); 153.96 ($CN\underline{C}O$); 166.93 ($C^-\underline{C}ON$)	1.21 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.1$); 1.51 (dd, 9 H, $CH_3CHC\underline{H}_3$, $^3J_{P,H} = 15.2$, $^3J_{H,H} = 7.2$); 1.52 (dd, 9 H, $C\underline{H}_3CHCH_3$, $^3J_{P,H} = 15.2$, $^3J_{H,H} = 7.2$); 2.77 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.4$, $^3J_{H,H} = 7.2$); 3.23 (dd, 1 H, $PC\underline{H}_aH_b$, $^2J_{H,H} = 15.5$, $^3J_{P,H} = 7.7$); 3.38 (dd, 1 H, $PCH_a\underline{H}_b$, $^2J_{H,H} = 15.5$, $^3J_{P,H} = 7.7$); 4.20 (q, 2 H, $C\underline{H}_2CH_3$,$^3J_{H,H} = 7.1$); 6.55 (d, 1 H, Ph, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.2$); 7.39 (t, 1 H, Ph, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.2$); 7.52 (td, 1 H, Ph, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.3$); 7.74 (d, 1 H, Ph, $^3J_{H,H} = 7.9$)	40.98
6j	14.58 ($CH_2\underline{C}H_3$); 17.15 (d, $(\underline{C}H_3)_2CH$, $^2J_{P,C} = 3.3$); 17.90 (d, CH_2P, $^1J_{P,C} = 43.9$); 20.79 (d, $(CH_3)_2\underline{C}H$, $^1J_{P,C} = 40.1$); 50.24 (d, $\underline{C}CH_2P$, $^2J_{P,C} = 4.2$); 55.79 ($O\underline{C}H_3$); 61.27 ($\underline{C}H_2CH_3$); 126.84 ($\underline{C}N$); 155.76 ($N\underline{C}OO$); 168.25 ($^-C\underline{C}ON$); 111.99, 120.37, 127.86, 128.55 (CHPh); 129.59, 154.35 ($\underline{C}Ph$)	1.14 (t, 3 H, $C\underline{H}_3CH_2$,$^3J_{H,H} = 7.1$); 1.39 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H} = 15.1$, $^3J_{H,H} = 7.2$); 2.65 (d.sept, 3 H, $C\underline{H}_2CH_3$, $^2J_{P,H} = 12.5$, $^3J_{H,H} = 7.2$); 3.17 (br.d, 2 H, $C\underline{H}_2P^+$, $^2J_{P,H} = 8.1$); 3.77 (s, 3 H, $OC\underline{H}_3$); 4.11 (q, 2 H, $C\underline{H}_2CH_3$ $^3J_{H,H} = 7.1$); 6.81 (t, Ph, $^3J_{H,H} = 7.6$, $^3J_{H,H} = 7.6$); 6.83 (d, 1 H, Ph, $^3J_{H,H} = 7.6$); 7.11 (td, 1 H, Ph, $^3J_{H,H} = 7.6$, $^3J_{H,H} = 7.6$, $^4J_{H,H} = 1.4$); 7.28 (dd, 1 H, Ph, $^3J_{H,H} = 7.6$, $^4J_{H,H} = 1.4$)	40.97
8	14.75 ($OCH_2\underline{C}H_3$); 17.15 (d, $(\underline{C}H_3)_2CH$, $^2J_{P,C} = 2.8$); 17.78 (d, CH_2P, $^1J_{P,C} = 43.8$); 18.42 (CH_3); 20.82 (d, $(CH_3)_2\underline{C}H$, $^1J_{P,C} = 40.1$); 50.48 (d, $\underline{C}CH_2P$, $^2J_{P,C} = 4.0$); 61.41 ($\underline{C}H_2CH_3$); 127.05 ($\underline{C}N$); 126.61, 127.82, 131.28, 136.42 ($\underline{C}HPh$); 136.46, 136.61 ($\underline{C}Ph$); 154.19 ($N\underline{C}OO$); 168.27 ($C\underline{C}ON$)	1.25 (t, 3 H, $CH_2C\underline{H}_3$, $^3J_{H,H} = 7.1$); 1.55 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{P,H} = 15.1$, $^3J_{H,H} = 7.2$); 2.38 (s, 3 H, CH_3); 2.74 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^2J_{P,H} = 12.5$, $^3J_{H,H} = 7.2$); 3.25 (br.d, $C\underline{H}_2P^+$, $^2J_{P,H} = 8.0$); 4.21 (q, 2 H, $C\underline{H}_2CH_3$, $^3J_{H,H} = 7.1$); 6.96 (d, 1 H, Ph, $^3J_{H,H} = 7.9$, $^4J_{H,H} = 1.9$); 7.03 (br.s, 1 H, Ph, $^4J_{H,H} = 1.9$); 7.32 (d, 1 H, Ph, $^3J_{H,H} = 7.9$)	41.01

* ^{19}F NMR spectrum, δ: –60.36 (CF_3).

Carbamate 6g. A mixture of zwitterion **1a** (0.3 g, 0.001 mol) and 2-isopropylphenyl isocyanate (0.68 g, 0.0042 mol) in $CHCl_3$ (0.5 mL) was kept at 60 °C for 13 h. The reaction mixture was treated as described above. Compound **6g** was obtained as a colorless powder.

Carbamates 6j and 10. A mixture of zwitterion **1a** (0.5 g, 0.0017 mol) and the corresponding isocyanate (5 equiv.) in CH_2Cl_2 (0.5 mL) was kept in a closed vessel at ~20 °C for 50 days. Then the reaction mixture was added dropwise with stirring to Et_2O (50 mL). The flocculent precipitates that formed were filtered off and crystallized repeatedly from a $Me_2CO—Et_2O$—hexane mixture to obtain a colorless powder (**6j**) and colorless crystals (**10**).

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